

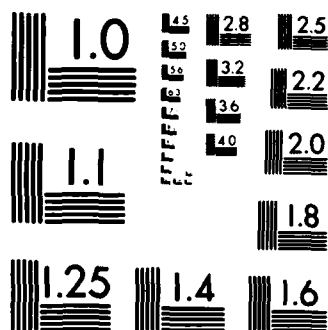
ELECTROCHEMISTRY OF FERROCENE IN

1-METHYL-3-ETHYLIMIDAZOLIUM CHLORIDE/ALU.. (U) FRANK J  
SEILER RESEARCH LAB UNITED STATES AIR FORCE ACADEMY C..

UNCLASSIFIED

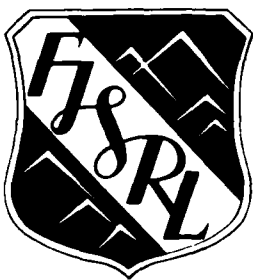
SEILER RESEARCH LAB UNITED STATES AIR FORCE ACADEMY  
B J PIERSMA ET AL. AUG 86 FJSRL-TR-86-0005 F/G 7/4

ML



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A171 448



FJSRL-TR-86-0005

FRANK J. SEILER RESEARCH LABORATORY

**ELECTROCHEMISTRY OF FERROCENE IN  
1-METHYL-3-ETHYLIMIDAZOLIUM CHLORIDE/ALUMINUM  
CHLORIDE ROOM TEMPERATURE MELTS**

B. J. PIERSMA

J. S. WILKES

DTIC  
ELECTE  
AUG 27 1986  
E

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED.

August 1986

**AIR FORCE SYSTEMS COMMAND  
UNITED STATES AIR FORCE**

DTIC FILE COPY



FJSRL-TR-86-0005

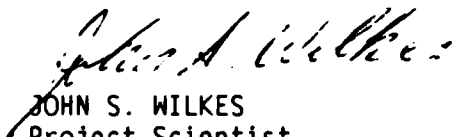
This document was prepared by the Electrochemistry Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO. The research was conducted under Project Work Unit number 2303-F2-10. Dr. John S. Wilkes was the project scientist.


When U.S. Government drawings, specifications, or other data are used for any purpose other than a definitely related government procurement operation, the government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the government may have formulated, furnished or in any way supplied the said drawings, specifications or other data is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Inquiries concerning the technical content of this document should be addressed to the Frank J. Seiler Research Laboratory (AFSC), FJSRL/NC, USAF Academy, Colorado Springs, CO 80840. Phone AC 303-472-2655.

This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

  
JOHN S. WILKES  
Project Scientist

  
CHESTER J. DYMEK, JR., Lt Col, USAF  
Director, Chemical Sciences

KENNETH E. SIEGENTHALER, Lt Col, USAF  
Chief Scientist

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

Printed in the United States of America. Qualified requestors may obtain additional copies from the Defense Documentation Center. All others should apply to:

National Technical Information Service  
6285 Port Royal Road  
Springfield VA 22161

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

ADA 171 448

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) FJSRL-TR-86-0005			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Frank J. Seiler Research Lab		6b. OFFICE SYMBOL (If applicable) FJSRL/NC	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State and ZIP Code) USAF Academy Colorado Springs, CO 80840-6528			7b. ADDRESS (City, State and ZIP Code)		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State and ZIP Code)			10. SOURCE OF FUNDING NOS.		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
			6.1	2303	F2
11. TITLE (Include Security Classification) Electrochem of Ferrocene in 1-Methyl-3-Ethylimidazolium Chloride/			12. PERSONAL AUTHOR(S) Aluminum Chloride Rm Temp Melts B. J. Piersma and J. S. Wilkes		
13a. TYPE OF REPORT Tech. Report		13b. TIME COVERED FROM 1 Jun 86 to 25 Jul 86	14. DATE OF REPORT (Yr., Mo., Day) 86/07/25		15. PAGE COUNT 18
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB. GR.	Ferrocene, molten salt, chloroaluminate		
10	02				
07	04				
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>Ferrocene has been studied in 1-Me-3-EtImCl-AlCl<sub>3</sub> melts over a range of Lewis acidities by varying the melt composition from 0.4 to 0.6 (mole fraction of AlCl<sub>3</sub>). The redox potential for ferrocene is not influenced by chloride concentration in the melts and is 0.40 ± 0.005 V (vs Al in 0.6 melt). Ferrocene is stable in basic and neutral melts but reacts chemically in acidic melts. Kinetic studies show the chemical reaction to be second order with a rate constant of about <math>9 \times 10^{-5}</math> 1/M sec, at 27C. The reversible redox processes were studied using cyclic voltammetric, steady-state potentiostatic and rotating disk electrode voltammetry at glassy carbon electrodes. Kinetic parameters indicate the electrode processes to be kinetically controlled and the rate limiting step is a chemical process following the electron transfer for both oxidation and reduction.</p>					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/>			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL John S. Wilkes			22b. TELEPHONE NUMBER (Include Area Code) (303) 472-2655		22c. OFFICE SYMBOL FJSRL/NC

ELECTROCHEMISTRY OF FERROCENE IN  
1-METHYL-3-ETHYLIMIDAZOLIUM CHLORIDE/ALUMINUM  
CHLORIDE ROOM TEMPERATURE MELTS

By

B. J. Piersma

J. S. Wilkes

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

August 1986

Approved for public release; distribution unlimited



Directorate of Chemical Sciences  
The Frank J. Seiler Research Laboratory  
Air Force Systems Command

## TABLE OF CONTENTS

Summary . . . . .	1
Preface . . . . .	11
List of Tables . . . . .	111
Introduction . . . . .	1
Experimental . . . . .	2
Results and Discussion . . . . .	2
Conclusions . . . . .	6
References . . . . .	9
Abbreviations . . . . .	11
List of Illustrations . . . . .	12

## SUMMARY

Ferrocene has been studied in 1-Me-3-EtImCl-AlCl<sub>3</sub> melts over a range of Lewis acidities by varying the melt composition from 0.4 to 0.6 (mole fraction of AlCl<sub>3</sub>). The redox potential for ferrocene is not influenced by chloride concentration in the melts and is  $0.40 \pm 0.005$  V (vs Al in 0.6 melt).

Ferrocene is stable in basic and neutral melts but reacts chemically in acidic melts. Kinetic studies show the chemical reaction to be second order with a rate constant of about  $9 \times 10^{-5}$  l/M sec, at 27°C. The reversible redox processes were studied using cyclic voltammetric, steady-state potentiostatic and rotating disk electrode voltammetric techniques at glassy carbon electrodes. Kinetic parameters indicate the electrode processes to be kinetically controlled and the rate limiting step is a chemical process following the electron transfer for both oxidation and reduction.



## PREFACE

The work described in this report was initiated in the Electrochemistry Task at the Frank J. Sellar Research Laboratory when B. J. Piersma was a visiting professor from Houghton College, Houghton, NY in 1981-1982 under the University Resident Research Program of the Air Force Office of Scientific Research. This report was completed when B. J. P. participated in the Summer Faculty Research Program sponsored by the Air Force Office of Scientific Research/AFSC, United States Air Force, under contract F49620-85-C-0013.

## LIST OF TABLES

1. Summary of Rotating Disc Electrode Experiments.
2. Cyclic Voltammetric parameters for Ferrocene.

## INTRODUCTION

Electrochemical studies of transition metal cations in a new room temperature molten salt system have shown that ion complexation and hence transport and kinetic behavior are strongly dependent on the Lewis acidity of the melt.(1) The melt acidity is widely variable by changing the mole ratio of aluminum chloride to 1-methyl-3-ethylimidazolium chloride from 0 to 2. Here we express the melt composition as apparent mole fraction  $\text{AlCl}_3$  (N). Ferrocene (bis(cyclopentadienyl)iron) was chosen for this study because it should not be dependent on the melt acidity, i.e., should not be influenced by the chloride ion concentration of the melt.

In a brief communication, Osteryoung, et al. indicated that ferrocene undergoes a reversible one-electron redox process in N=0.67 aluminum chloride - ethylpyridinium bromide melt.(2) The  $E_{p/2}$  was found to be 0.25V with reference to Al wire in acidic melt. In a more detailed study of ferrocene and ferricenium ion in butylpyridinium melt, Osteryoung, et al. showed that ferrocene is stable in basic and neutral melts and ferricenium ion is stable in neutral and acidic melts.(3) In that work it was suggested that ferrocene is oxidized by traces of oxygen in the melt.

This report presents our study of ferrocene in  $\text{MeEtImCl}/\text{AlCl}_3$  melts at approximately 25C, with emphasis on reaction kinetics. Cyclic voltammetric and steady-state potentiostatic techniques were used to determine kinetic parameters for the redox processes of ferrocene at a glassy carbon electrode. Rotating disk electrode voltammetry was used to follow the chemical reaction of ferrocene in acidic melt.

## EXPERIMENTAL

The experimental details have been previously reported.(4) Measurements were made with a polished Pine Instruments Co. glassy carbon electrode. A large tungsten foil was used a counter electrode and the reference was an Al wire immersed in N=0.6 melt. Other details are as previously discussed.(4)

## RESULTS AND DISCUSSION

The electrochemical window in neutral N=(0.50) melt from +2.30V to -1.6V is presented in Fig. 1. Also shown in Fig. 1 is the reversible redox couple for Ferrocene in neutral melt. The redox couples and melt limits are given in Fig. 2 for Ferrocene in basic, neutral, and acidic melts. The average value of  $E_{p/2}$  for melts from N=0.4 to 0.6 is  $+0.403 \pm 0.005V$  vs Al wire in 0.6 melt. Thus the Ferrocene redox couple appears to be unaffected by the chloride concentration of the melt.

### Chemical Reaction of Ferrocene

Yellow solutions of Ferrocene in neutral and basic melts were stable for at least two weeks (the length of time observations were made). This was demonstrated by obtaining identical limiting currents at a rotating glassy carbon electrode over this period of time. Greenish-yellow solutions of Ferrocene obtained initially in acidic melts turned dark blue after standing 6-8 hours. Assuming that the limiting current for Ferrocene oxidation is proportional to the Ferrocene concentration in the melt, the reaction of

Ferrocene with acidic melt was followed by measuring limiting currents as a function of time. The linear variations of  $1/i$  vs time for Ferrocene, given in Fig. 3, indicates that the variation is 2nd order in Ferrocene. The rate constant is approximately  $9 \times 10^{-5}$  l/M sec. This may be compared with the rate constants determined for the reaction of  $\text{Fe}^{3+}$  with acidic melt of  $5.9 \times 10^{-5}$  l/M sec obtained for a range of concentrations of  $\text{FeCl}_3$  from 0.03 to 0.155 M, and for the reaction of  $\text{Cu}^{2+}$  with acidic melt of  $5.1 \times 10^{-4}$  l/M sec. The reaction of Ferrocene with acidic melt may be a completely different process than that for  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  since the  $\text{Fe}^{2+}$  in Ferrocene would be oxidized if it is the reacting species, while  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  must be reduced. Osteryoung has suggested that Ferrocene is oxidized to Ferricenium ion in acidic melt by traces of oxygen. (3) This remains an interesting question and could be the subject of another study.

#### RDE Studies

The anodic oxidation of Ferrocene is kinetically controlled, as demonstrated by plots of  $1/i$  vs  $\omega^{-1/2}$  (Fig. 4), but approaches diffusion limitations at higher overpotentials. The slopes of these plots were used to determine heterogeneous rate constants according to the expression

$$\frac{1}{i} = \frac{1}{nFK_f C_R} + \frac{1.61 \nu^{1/6}}{nF D_R^{3/2} C_R \omega^{1/2}} \quad (1)$$

Standard heterogeneous rate constants were obtained by plotting  $k_f$  vs  $E$  with extrapolations to  $E = E_p/2$ , using the relationship

$$k_f = k_s e^{-\alpha\eta Fe/RT} \quad (2)$$

The results for  $k_s$  and  $\alpha\eta$  are summarized in Table I.

The Levich equation

$$i_{d,a} = 0.620 nFA D_R^{2/3} \omega^{1/2} \nu^{-1/6} C_R \quad (3)$$

was used to calculate diffusion coefficients along with slopes from  $i$  vs  $\omega^{1/2}$  plots (Fig. 5) for high overpotentials where diffusion control is obtained. The values of the diffusion coefficients reported here (Table I) for Ferrocene in MeEtImCl melts at 25C are about 50% lower than those reported in Butylpyridinium melts at 40C by Osteryoung, et al. (3). The difference we observed in diffusion coefficients for neutral and acidic melts may be the result of a change in concentration from the initial concentration of Ferrocene in acidic melt by reaction of Ferrocene with the melt.

For the reversible Ferrocene redox couple, the number of electrons involved in the oxidation process was calculated from the slope of  $E$  vs  $\log (\frac{i_d - i}{i})$  plots (Fig. 6) according to the equation

$$E = E_{p/2} + \frac{RT}{nF} \ln \left( \frac{i_d - i}{i} \right). \quad (4)$$

As expected, one electron is involved in the anodic process irrespective of melt acidity.

## Cyclic Voltammetric Studies

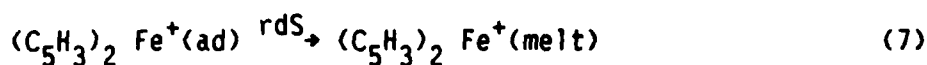
Detailed CV studies of the reversible Ferrocene redox couple were carried out in basic (0.4) and acidic (0.6) melts with sweep rate variation from 1 to 500 mV/sec. The parameters are summarized in Table II. The Tafel slope was unchanged by melt composition and is equivalent to  $b = RT/F$  for oxidation and  $b = -RT/F$  for reduction. This suggests that the redox mechanism for the Ferrocene couple is not dependent on the chloride concentration of the melt.

## Steady-state Studies

Steady-state potentiostatic  $E$  vs  $\log i$  curves for the anodic oxidation of Ferrocene are represented in Fig. 7, for basic (0.4) and acidic (0.6) melts. A linear  $E$  vs  $\log i$  plot with a slope equivalent to  $RT/F$  was obtained in basic melt over two decades of current. In acidic melt over a slightly smaller current range the Tafel slope was also  $RT/F$ . The higher limiting current observed in acidic melt is expected due to the lower viscosity and higher diffusion coefficient of the acidic melt (note that in Fig. 7 the Ferrocene concentration in acidic melt is 1.5 that in basic melt). When the concentration differences of Ferrocene are taken into account, assuming first order kinetics, comparison of steady-state currents at a given potential in the Tafel region shows that the reaction rate for Ferrocene oxidation is essentially independent of melt composition. Tafel slopes of  $RT/F$  for anodic oxidation and  $-RT/F$  for cathodic reduction obtained from CV measurements are consistent with steady-state results. It appears that although the structure and physical properties of the MeEtImCl melts undergo significant changes with

change in melt composition from basic to acidic conditions, the redox processes of Ferrocene are essentially independent of melt composition.

For  $n=1$  and  $\alpha=0.5$ , and assuming that adsorption of Ferrocene is not potential dependent, a Tafel slope of  $RT/F$  indicates that a step following a reversible electron transfer is the rate limiting step. For the anodic process, desorption of Ferricenium ion is a possible rate limiting step. Thus



For the cathodic reduction of Ferricenium ion, the reverse of steps 5-7 with desorption of Ferrocene as the slow step is a possible mechanism that satisfies the kinetic requirements.

## CONCLUSIONS

1. Ferrocene undergoes a reversible one-electron redox process in MeEtImCl/ $\text{AlCl}_3$  melts which is not influenced by the Lewis acidity (i.e., chloride ion concentration) of the melt.



2. Kinetic parameters derived from cyclic voltammetric and steady-state potentiostatic measurements indicate that a step following electron transfer is rate limiting (in the Tafel region) both for the oxidation of ferrocene and the reduction of ferricenium ion. Desorption is suggested as a possible rate limiting step for both oxidation and reduction.

3. Comparison of steady-state currents at a given potential in the Tafel region for ferrocene oxidation in basic and acidic melts indicates that the reaction rate is not influenced by melt composition. The standard heterogeneous rate constants from rotating disk measurements support this conclusion.

4. Ferrocene reacts chemically with acidic melts by a process that appears to be second order in ferrocene. Ferrocene is stable in basic and neutral melts.

TABLE I

## Summary of RDE Experiments

## Diffusion Coefficients

<u>Melt</u>	<u><math>D \times 10^7</math> (cm<sup>2</sup>/sec)</u>
0.500	4.3
basic (0.45)	3.5
acidic (0.55)	4.1

## Electrons of Anodic Oxidation

<u>Melt</u>	<u><math>n</math></u>
0.500	1
basic (0.40)	1
basic (0.45)	1
acidic (0.55)	1

## Kinetic Constants

<u>Melt</u>	<u><math>k_s \times 10^4</math> (cm/sec)</u>	<u><math>\alpha n</math></u>
0.50	7.3	0.6
basic (0.45)	~7.3	0.5
acidic	~7.3	0.55

## REFERENCES

1. B. J. Piersma and J. S. Wilkes, FJSRL-TR-82-0004, September 1982.
2. H. L. Chum, V. R. Koch, L. L. Miller, and R. A. Osteryoung, J. Am. Chem. Soc., 97, 3264 (1975).
3. Z. J. Karpinski, C. Nanjundiah, and R. A. Osteryoung, Inorg. Chem., 23, 3358 (1984).
4. J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, Inorg. Chem., 21, 1263 (1982).

TABLE II

## CV Parameters for Ferrocene

	$E_p/2$ (volts)	$\Delta E_p$ (mv)	$\frac{i_{p,a}}{i_{p,c}}$	$\frac{i_{p,c}}{v^{1/2}}$	$\frac{i_{p,a}}{v^{1/2}}$	$\frac{d(E_p/2 - E_{p,c})}{d \log i_c}$	$\frac{d(E_{p,a} - E_p/2)}{d \log i_a}$	$\frac{dE_{p,c}}{d \log v}$	$\frac{dE_{p,a}}{d \log v}$
0.4 melt	0.400	86	1.08	-const	-const	-60mv	60mv	-14mv	15mv
0.6 melt	0.406	84	1.07	-const	-const	-60mv	60mv	-12mv	13mv

### ABBREVIATIONS

$\alpha$	transfer coefficient
$b$	Tafel slope
cv	cyclic voltammetry
$D$	diffusion coefficient
$E_{p,a}$	potential (in volts) of anodic current peak
$E_{p,c}$	potential (in volts) of cathodic current peak
$\Delta E_p$	$(E_{p,a} - E_{p,c})$
$E_{p/2}$	$(E_{p,a} - E_{p,c})/2$
$i$	total current in $\mu$ amps/cm <sup>2</sup>
$i_d$	diffusion limited current density
$i_{p,a}$	current in ( $\mu$ amps) at the anodic current peak
$i_{p,c}$	current in ( $\mu$ amps) at the cathodic current peak
$k_s$	standard heterogenous rate constant
$n$	number of electrons
RDE	rotating disc electrode
rds	rate determining step
$v$	sweep rate (in mv/sec) for CV measurements
$\omega$	rotation rate (in radius/sec) for RDE

## ILLUSTRATIONS

Figure 1: Cyclic Voltammograms in Neutral (0.500) melt

- a.  $N=0.500$  melt  
 $v=100$  mv/sec,  $V=250$  mv/cm (horizontal),  $i=25$   $\mu$ A/cm (vertical),  
sweep limits are  $+2.30V$  (left) to  $-1.60V$  (right), initial  
potential is  $+0.20V$ .
- b.  $2.0 \times 10^{-2}M$  ferrocene in neutral melt. Parameters are the same  
as (a) except sweep limits are  $+1.70V$  to  $1.2V$  and the initial  
potential is  $+0.10V$ .

Figure 2: Cyclic Voltammograms for  $2 \times 10^{-2}M$  ferrocene.

- a. basic (0.45) melt.  
 $v=100$  mv/sec,  $V=250$  mv/cm,  $i=25$   $\mu$ A/cm, limits are  $+1.1V$  to  
 $-1.9V$ ,  $+0.10V$  initial potl.
- b. neutral (0.50) melt.  
 $v=100$  mv/sec,  $V=250$  mv/cm,  $i=50$   $\mu$ A/cm, limits are  $+1.9V$  to  
 $-1.35V$ ,  $+0.10V$  initial potl.
- c. acidic (0.55) melt.  
 $v=100$  mv/sec,  $V=250$  mv/cm,  $i=25$   $\mu$ A/cm, limits are  $+1.95V$  to  
 $-0.35V$ ,  $+0.20V$  initial potl.

Figure 3: Chemical Reaction of Ferrocene in Acidic Melt.

$2.0 \times 10^{-2} \text{M}$  ferrocene in 0.55 melt.

Figure 4:  $1/i$  vs  $\omega^{-1/2}$  curves for  $2.0 \times 10^{-2} \text{M}$  Ferrocene in 0.55 Melt.

Figure 5:  $i$  vs  $\omega^{1/2}$  curves at  $V=+0.70\text{V}$  in basic (0.45), neutral (0.50) and acidic (0.55) melts for  $2.0 \times 10^{-2} \text{M}$  Ferrocene.

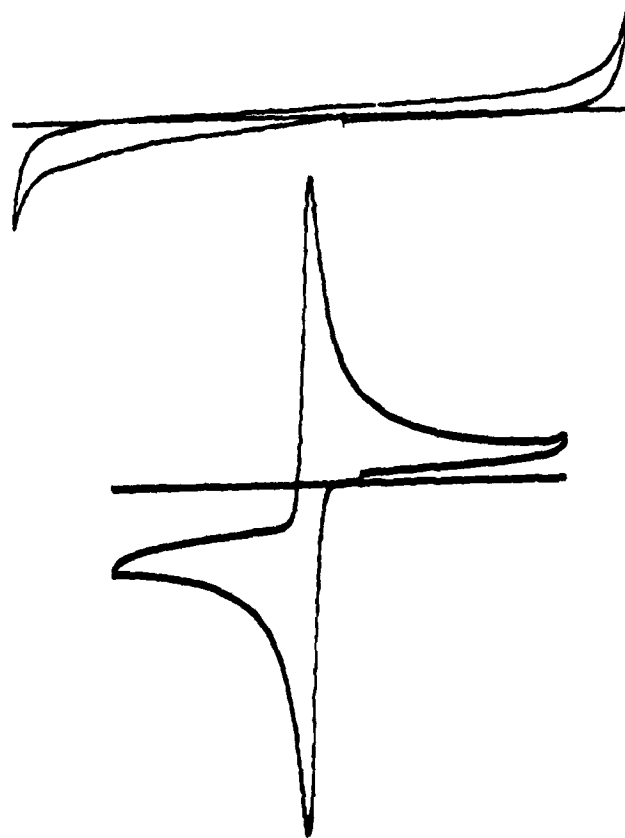
Figure 6:  $E$  vs  $\log \left( \frac{i_d - i}{i} \right)$  curves for  $2.0 \times 10^{-2} \text{M}$  Ferrocene in neutral, basic, and acidic melts.

Figure 7: Steady-state  $E$  vs  $\log i$  curves for Ferrocene

(●)  $1.5 \times 10^{-2} \text{M}$  Ferrocene in  $N=0.4$  melt

(□)  $2.3 \times 10^{-2} \text{M}$  Ferrocene in  $N=0.6$  melt

**FIGURE 1**





**FIGURE 2**

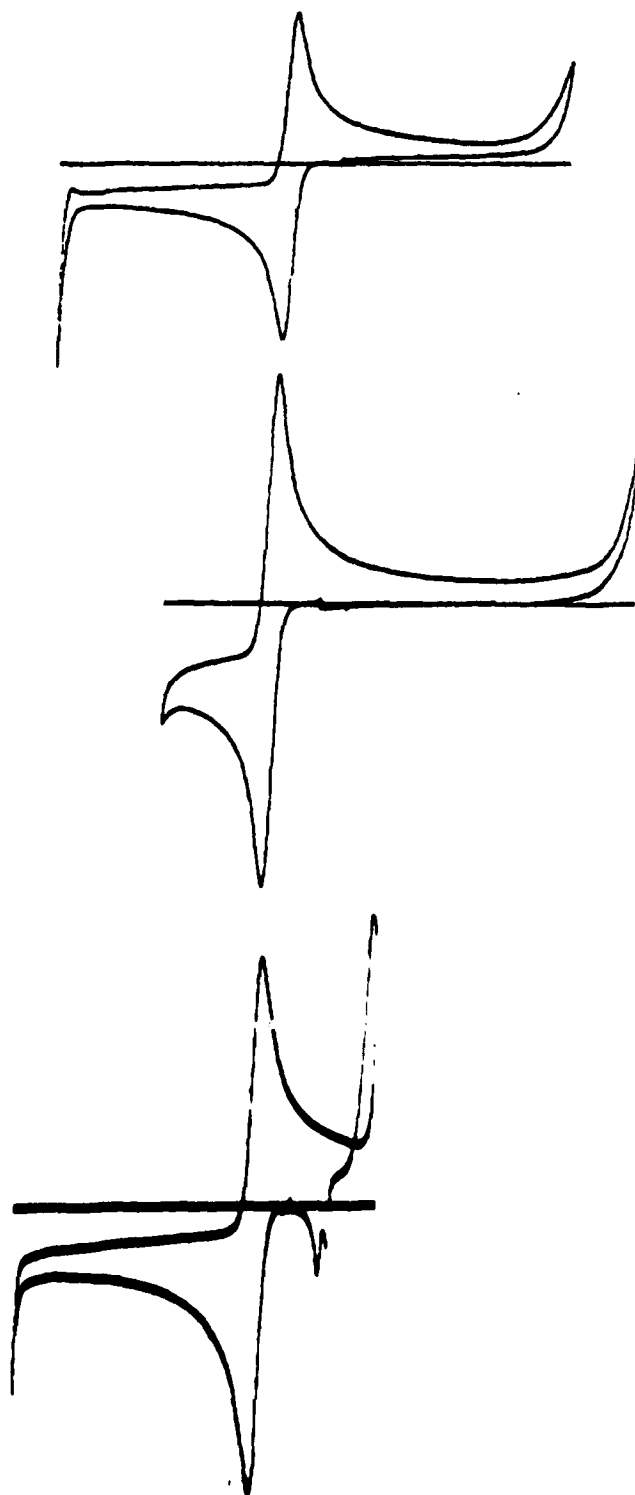


FIGURE 3

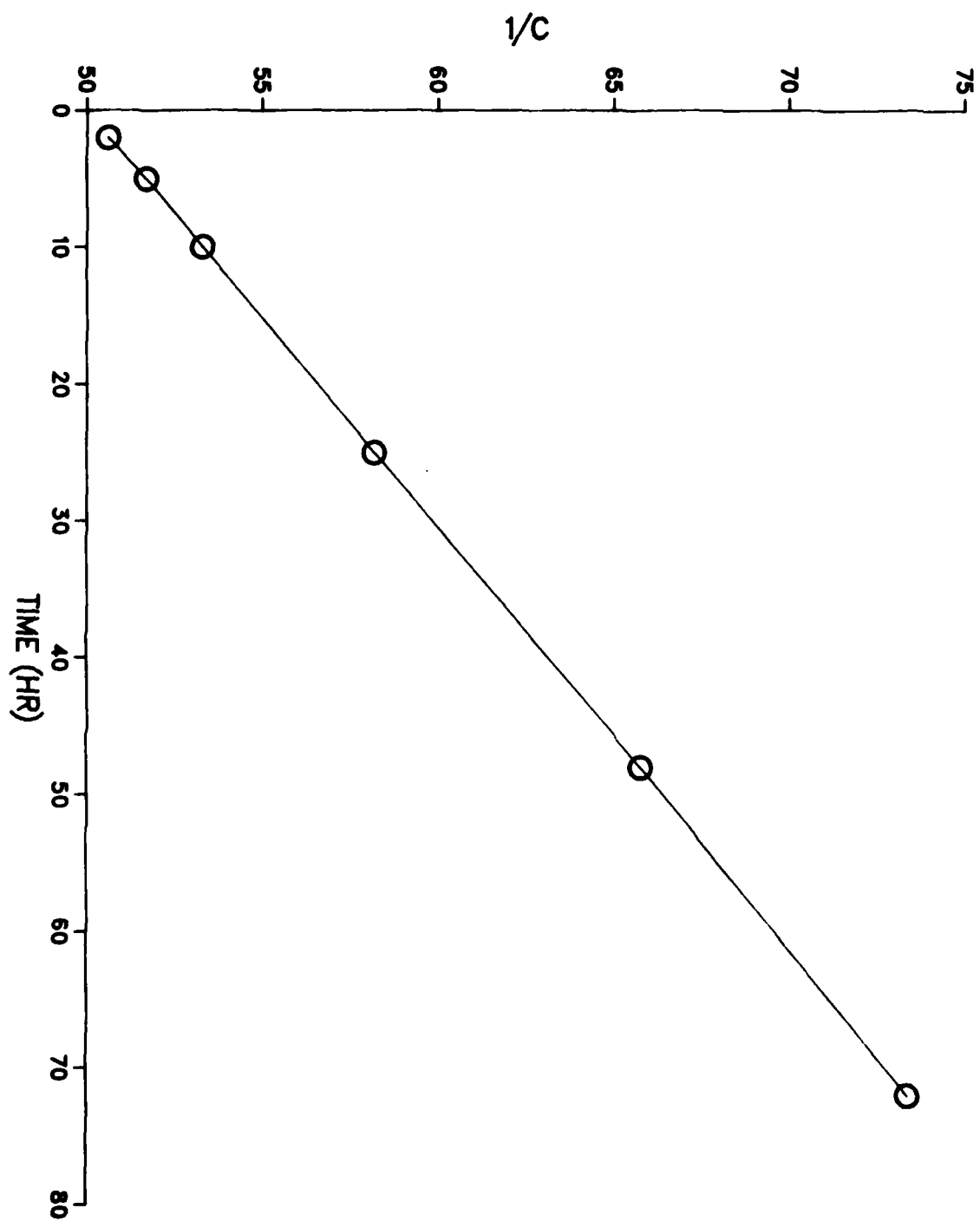


FIGURE 4

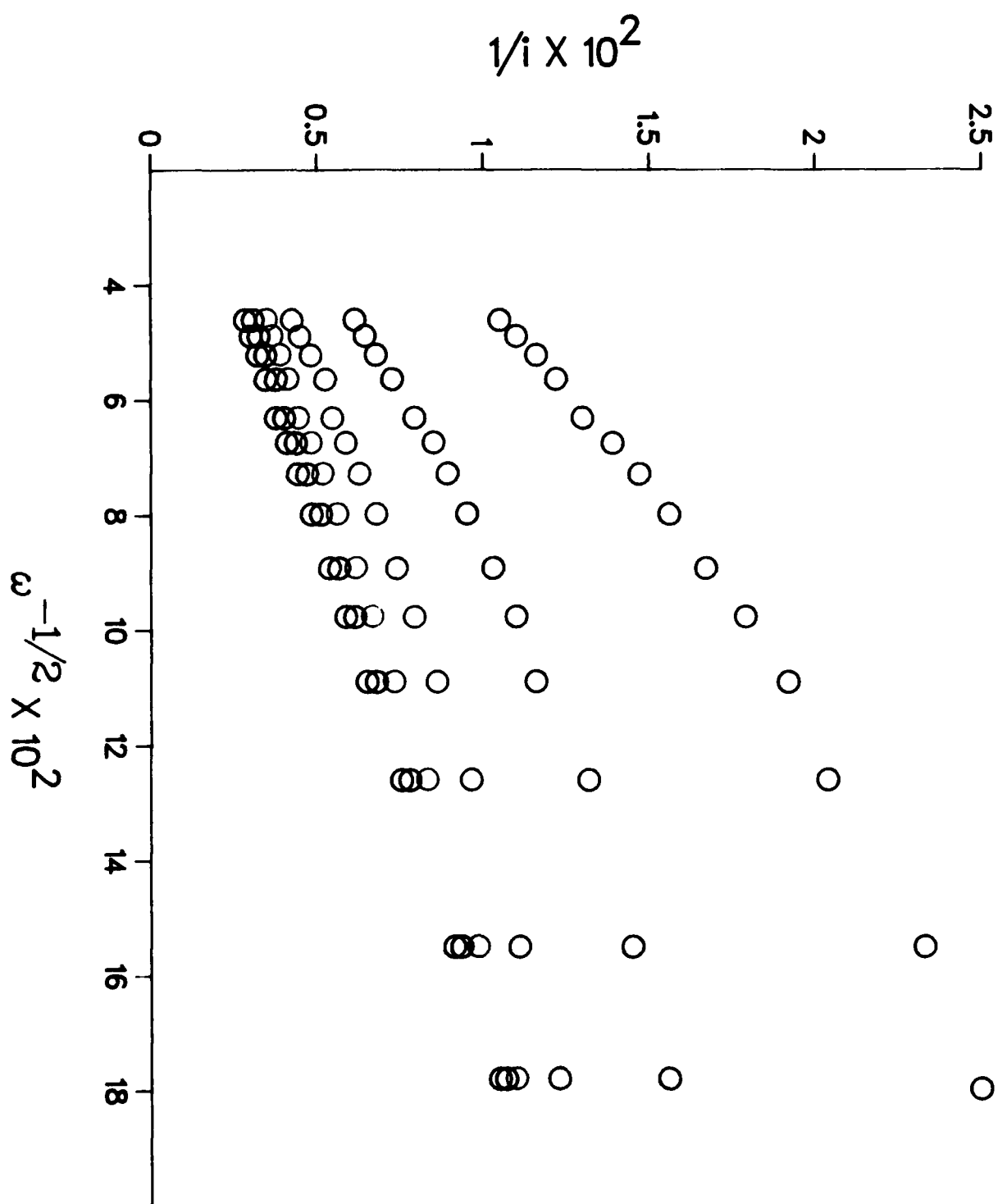


FIGURE 5

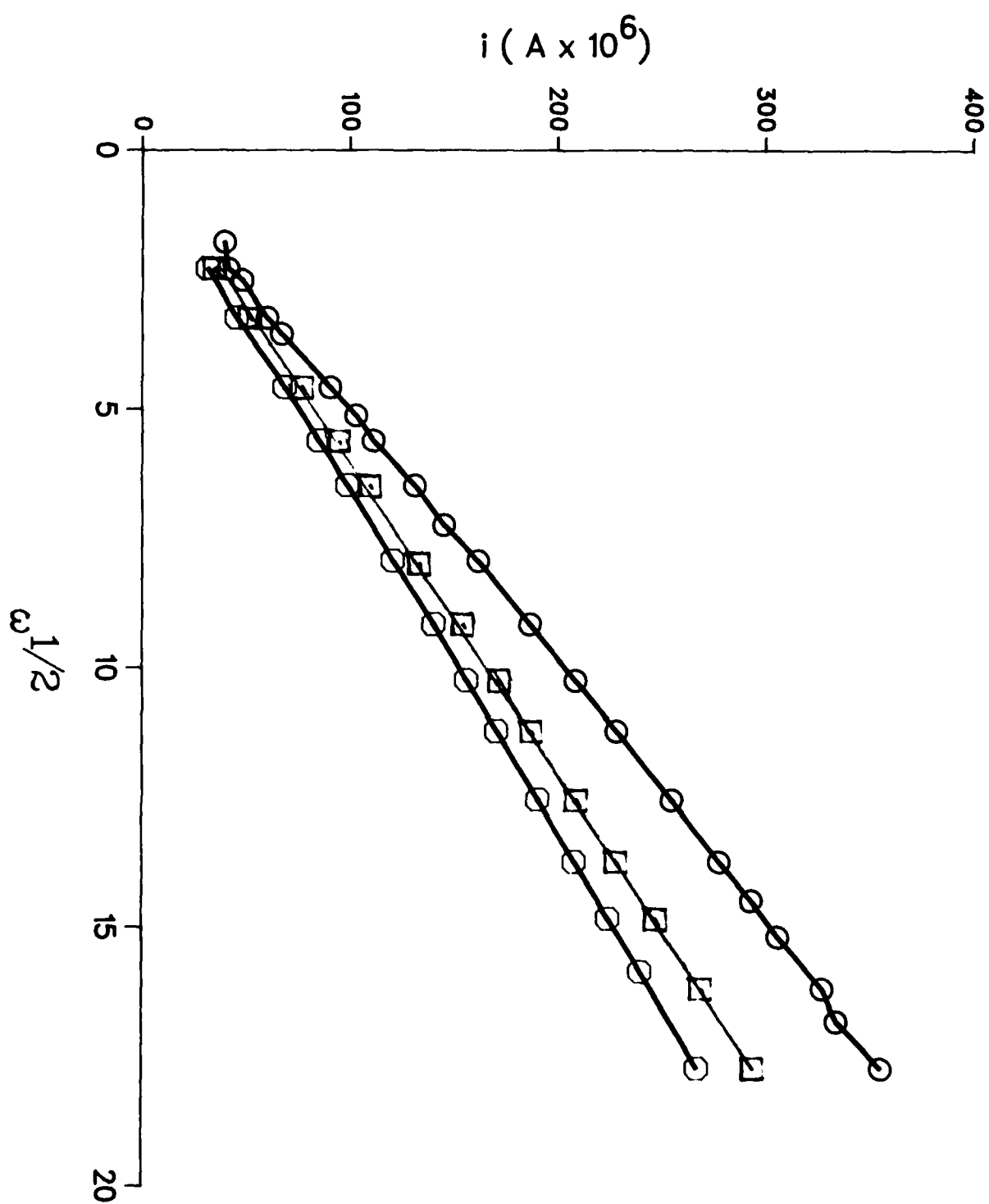


FIGURE 6

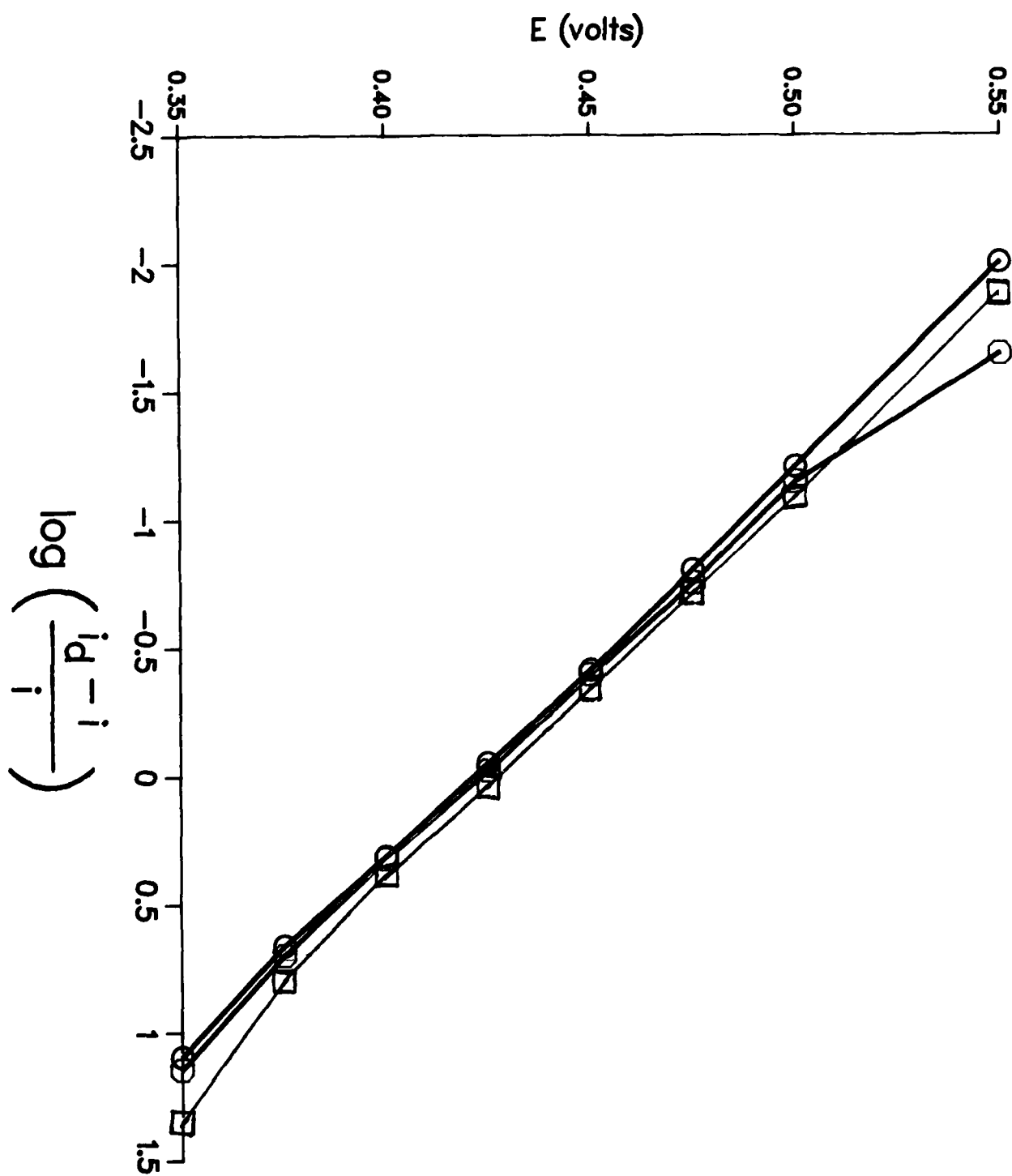
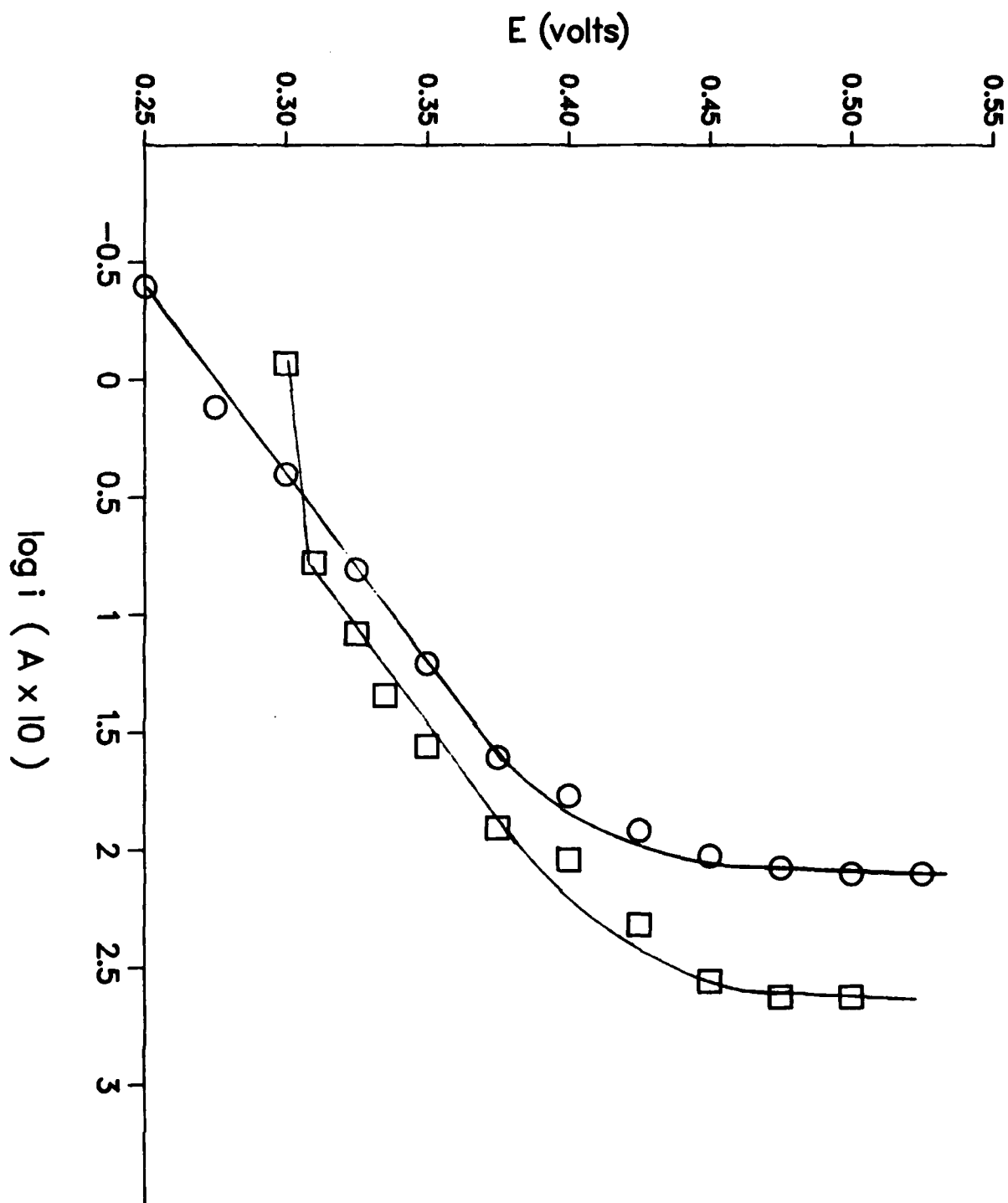


FIGURE 7



END

DTIC

10-86